Direct VOC Analysis of Water-Based Coatings By Gas Chromatography and Solid-Phase Microextraction

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Solvents in water-based coatings may be determined by sampling the coating head space using solid phase microextraction and gas chromatographing the extract. Several water-based coatings of known composition were analyzed by direct capillary gas chromatography and excellent agreement with theoretical VOC values was obtained. Fifty-two water-based architectural and industrial maintenance coatings were analyzed by a combination of SPME/GC and direct GC of solutions in methanol or dimethylformamide and the results compared with reported values. The SPME/GC method appears to be especially suitable for the analysis of low VOC content water-based coatings, for which EPA Method 24 often gives poor results. The identification and quantitation of exempt solvents may be performed easily with this method. Residual solvent in dried paint films may be determined by SPME/GC.

INTRODUCTION

The solvents found in most water-based architectural and industrial maintenance coatings are relatively pure, generally contain oxygen, and are relatively few in number in a given coating. The majority of commercial solvent-based architectural and industrial maintenance coatings, on the other hand, often contain different types of mineral spirits which are complex hydrocarbon mixtures composed of as many as several hundred individual components. These conclusions are drawn from a gas chromatographic (GC) examination of the solvents present in 52 water-based and 56 solvent-based air-drying architectural and industrial maintenance commercial coatings.[1]

Of the 52 water-based coatings studied, two contained a single solvent, 23 contained two solvents, 12 contained three solvents and the remainder contained four to six different solvents at concentrations of 0.1% or more (*Figure* 1). A list of the major solvents in the 52 coatings and the frequency with which each was found is given in *Table* 1. Many of the coatings were found to contain trace amounts (below 0.1%) of various volatile materials attributable to residual monomers in the resins used to manufacture the coatings, to non-polymerizable impurities in the monomers used to manufacture the resins, and to possible contamination incurred during coating manufacture.

Since the number of solvents in water-based coatings is small, these may be individually quantified and the total volatile organic compound (VOC) content may be determined directly. This strategy differs from the current EPA Method 24[2] (ASTM Practice D 3960)[3] in which total VOC content is determined by subtraction of the combined water content and nonvolatile content from a given weight of coating. This direct method may be advantageous in determining the VOC content of low VOC content coatings, especially in high water/low nonvolatile content coatings for which EPA Method 24 tends to be unreliable.[4]

The method used for the analysis of water-based coatings consists of a preliminary screening of the coating by solid-phase microextraction/gas chromatography (SPME/GC) followed by direct gas chromatography (GC) of a solution of the coating in methanol (MeOH) and/or dimethylformamide (DMF) containing an internal stan-

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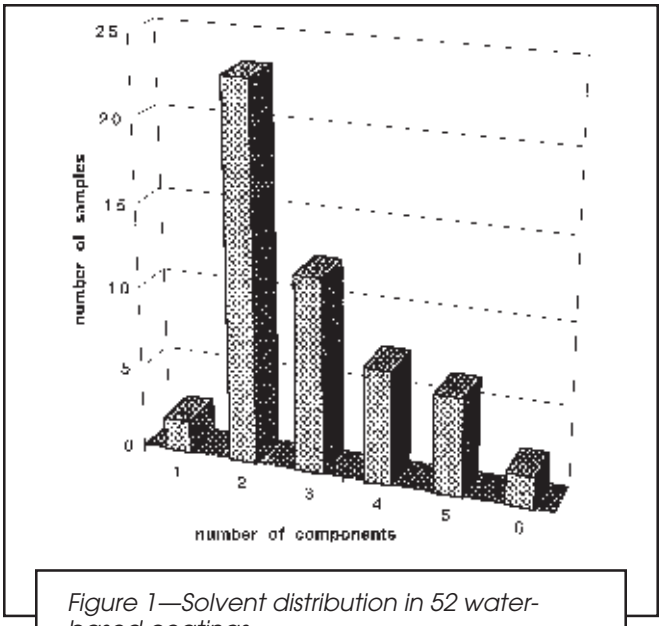

Figure 1—Solvent distribution in 52 water-based coatings.

dard. The SPME screening procedure serves several functions: (1) the solvents present in the coating, including very low concentrations of minor volatile contaminants, are identified; (2) the solvent, either MeOH, or DMF, or both, to be used for the direct GC analysis is determined; and (3) GC peaks formed by decomposition of solid coating materials in the hot injection port of the gas chromatography, in addition to those formed by solvent evaporation, during GC analysis of the coating solutions are identified.

A concern associated with EPA Method 24 involves the question of whether some high boiling solvents remain in the paint film after one hour of drying at 110°C. We undertook a study to evaluate the significance of this phenomenon for the solvents Texanol™, ethylene glycol, butyl carbitol, dibutyl phthalate, and dioctyl phthalate. Extraction of dried paint films containing Texanol, butyl carbitol, and dibutyl phthalate followed by gas chromatography of the extracts indicated that these three solvents are only partially lost under the conditions used for determining the nonvolatile content of the coating by ASTM Method D 2369.[5]

EXPERIMENTAL

Solid-Phase Microextraction

Solid-phase microextraction (SPME) is an alternative to traditional sample preparation techniques. Developed by Dr. Janusz Pawliszyn[6] at the University of Waterloo (Toronto, Canada), the method uses a fused silica fiber, coated with a suitable adsorbent, that is mounted on a modified GC syringe to extract samples and pass analytes directly into a heated GC injection port.[7] For the analysis of coating samples, approximately one gram of coating was placed into a 40 mL septum-top vial containing two grams of solid sodium chloride. The mixture was homogenized by stirring with a thin glass rod, capped, and let stand for 30 min. The salt removes the water in the coating by solvation and helps to free the organic solvents from bonding interactions with the water, allowing them to pass more easily into the vapor phase. The head space in the vial was then exposed to an SPME fiber coated to a thickness of 65 µm with Carbowax™ - Divinylbenzene for five minutes at room temperature. The coated fiber acts as a "sponge," concentrating the organic analytes on its surface so they can be transferred to the gas chromatograph. Following this sampling period, the fiber was withdrawn from the vial, and introduced into the heated injection port of the GC. In the injector, analytes are thermally desorbed and transferred to the GC column for analysis.

A solvent retention index library was established from 22 known solvents which might be expected to be found in water-based coatings. The solvents ranged in volatility from methanol/acetone to butyl carbitol/Texanol. The combined solvents were emulsified with 5% Triton X-200 at a concentration of 0.5% of each component. This mixture was sampled as described previously and chromatographed using a 30 m × 0.53 mm SE-30 capillary column. The instrument used for the analyses was a Hewlett-Packard Model 5890 gas chromatograph equipped with a capillary injector and flame ionization detector. It was used in the split mode, with an injection port temperature of 250°C. The flame ionization detector was maintained at 260°C. The oven was programmed from an initial temperature of 40°C for four minutes, followed by a 20°C per min ramp to 240°C. The final temperature was held for two minutes. The SPME chromatogram for this mixture is given in *Figure* 2. Other solvents were added to the library with subsequent SPME runs at concentrations ranging from 0.1 to 1.0%, emulsi-

Table 1—Solvents Found in 52 Water-Based Architectural and Industrial Maintenance Coatings and Frequency of Appearance

Component	Present in Samples
Texanol	37
Propylene glycol	31
Diethylene glycol butyl ether	23
Ethylene glycol	14
Ethylene glycol butyl ether	7
Isopropyl alcohol	5
Methanol	5
N-methylpyrrolidone	4
Dipropylene glycol methyl ether	3
Dibutyl phthalate	2
Diethylene glycol methyl ether	2
Ethanol	2
Propylene glycol butyl ether	2
2-Butanol	2
Aminomethylpropanol	2
Diethylene glycol ethyl ether	1
Diethylene glycol	1
Dipropylene glycol butyl ether	1
Glycerin	1
Hexylene glycol	1
Methyl amyl ketone	1
Propylene glycol methyl ether	1
Propylene glycol propyl ether	1

Texanol is the trade name for 2,2,4-trimethyl-1,3,pentanediol monoisobutyrate and is manufactured by the Eastman Chemical Co.

Table 2—Retention Index Library of Possible Solvents, Including Minor Components, for Various Water-Based Coatings as Determined by Solid Phase Microextraction (SPME)

Methanol (MEOH)	100
Ethanol (EtOH)	113
Acetone	123
Isopropyl alcohol (IPA)	127
Propyl alcohol (PA)	159
Methyl ethyl ketone (MEK)	183
2-butanol (2-BuOH)	194
Isobutyl alcohol (i-BuOH)	227
Butyl alcohol (BuOH)	281
Propylene glycol monomethyl ether (PM)	298
Triethylamine (TEA)	355
Ethylene glycol (EG)	376
Propylene glycol (PG)	445
Toluene	500
Ethylene glycol monopropyl ether (EP)	550
Propylene glycol monpropyl ether (PnP)[a]	598, 614
Ethylbenzene	621
Proplylene glycol monotert-butyl ether (PTB)	623
p and m-Xylene	631
Methyl amyl ketone (MAK)	642
Dibutyl ether	649
o-Xylene	653
Ethylene glycol monobutyl ether (EB)	661
Butyl propionate	662
Hexylene glycol (HG)	662
Diethylene glycol monomethyl ether (DM)	679
Propylene glycol monobutyl ether (PnB)[a]	695, 708
Diethylene glycol monoethyl ether (DE)	737
Dipropylene glycol monomethyl ether (DPM)[b]	738, 743, 751
N-Methylpyrrolidone (NMP)	755
2-Ethylhexanol (2-EH)	764
Dipropylene glycol (DPnG)b	771, 784, 786
Diethylene glycol monopropyl ether (DP)	804
Dipropylene glycol monopropyl ether (DPnP)[a]	846, 848
Diethylene glycol monobutyl ether (DB)	867
Ethylene glycol monophenyl ether (EPh)	884
Dipropylene glycol monobutyl ether (DPnB)[a]	903, 905
Ethylene glycol mono2-ethylhexyl ether (EEH)	903
Propylene glycol monophenyl ether (PPh)	903
Texanol (TX)[a]	973, 982
Diethylene glycol monohexyl ether (DH)	982
Tetradecane (C14)	1000

(a) Consists of two isomers and exhibits two GC peaks.
(b) Consists of three isomers and exhibits three GC peaks.

fied with 5% Triton X-200. The complete list of known solvents and associated retention indexes is given in *Table* 2. When unknown volatile materials were encountered in analyzing coatings samples, identification was established by carrying out an SPME/GC/mass spectrometry determination followed by FID comparison with the GC/MS identified authentic known material.

We chose to establish a retention index library, rather than a retention time library, because retention times reveal them to vary slightly from run to run and day to day due to small, unavoidable variations, such as column temperature and gas flow rates. A retention index is essentially a measure of the position, measured in arbitrary units, of an analyte peak between two known peaks separated by a distance measured in the same arbitrary units. For hydrocarbon mixtures, retention indexes are generally assigned with respect to the normal alkanes.[8] For solvents in water-based systems, we chose methanol, toluene, and tetradecane (C14) as reference solvents. Methanol was chosen because it is almost always the first GC peak to elute using an SE-30 (or equivalent non-polar phase) capillary column. Tetradecane, when added to a water-based coating, is almost always the last GC peak, eluting immediately after the double peak for Texanol which is found in many water-based coatings. Toluene gives a marker at mid-range of the elution spectrum. We have assigned an arbitrary value of 100 as the retention index to methanol, a value of 500 to toluene, and a value of 1000 to tetradecane. Thus, if an analyte has a retention index of 300, it elutes from the GC column at a time distance exactly midway between methanol and toluene.

To assign a retention index to a specific peak in the chromatogram of a sample, an initial SPME/GC screen was carried out to establish which GC peaks result from the solvents in the coatings. After this initial screen, the SPME fiber was placed into the head space of a 40 mL vial containing 2 mL of tetradecane, five drops of toluene, and five drops of methanol for approximately 10 sec. The fiber, now containing a small quantity of the retention index marker compounds, was then used to sample the coating head space a second time and a new chromatogram containing the markers and coating solvents was obtained. The equations used for calculating retention indexes are:

$$RI_{analyte} = 100 + 400\left[\frac{(t_{analyte} - t_{MeOH})}{(t_{toluene} - t_{MeOH})}\right]$$

for solvents which elute after methanol but before toluene, where t is retention time, and,

$$RI_{analyte} = 500 + 500\left[\frac{(t_{analyte} - t_{toluene})}{(t_{C14} - t_{toluene})}\right]$$

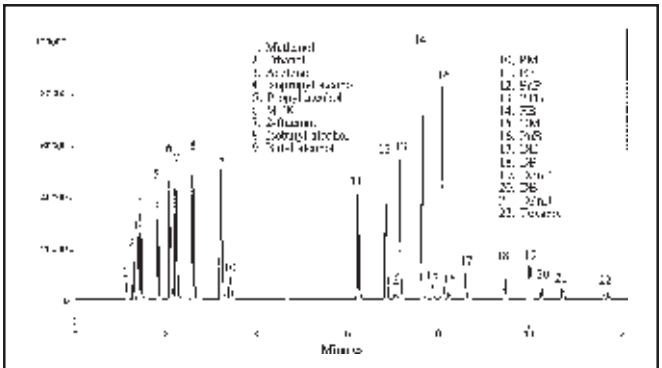

Figure 2—SPME chromatogram of some common solvents found in water-based coatings.

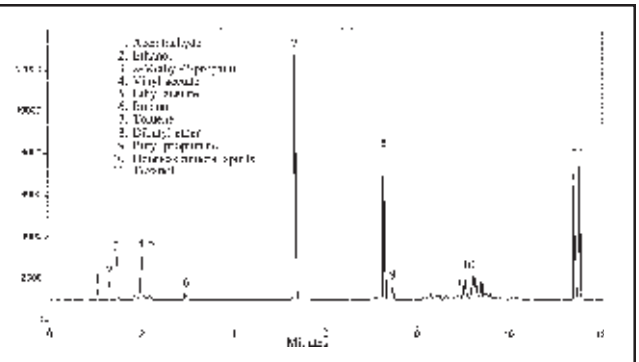

Figure 3—SPME chromatogram of a commercial vinyl-acrylic latex spiked with 2% Texanol, 0.05% toluene, and 0.05% odorless mineral spirits.

for solvents which elute after toluene but before tetradecane (C14).

In screening coatings by the SPME procedure, it was found that low boiling solvents and water-insoluble solvents gave very strong SPME responses, i.e., were easily transported into the vapor phase and strongly adsorbed by the fiber coating. Thus, very low concentrations of compounds such as acetaldehyde, ethyl acetate, vinyl acetate, toluene, ethylbenzene, xylene, dibutyl ether, butyl propionate, and mineral spirits, which might not be detected by direct chromatography of coatings solutions, may be detected by the SPME procedure. Dibutyl ether and butyl propionate, for example, were found in most paints containing acrylic resins and in the acrylic resins alone. Since the concentrations of these analytes were quite low in sampled coatings, it is likely that these solvents originate as non-polymerizable impurities in the butyl acrylate used in the manufacture of the resins. The small concentrations of hydrocarbons found in some coatings probably also originate with the resin used to manufacture the coating or to additives such as defoamers. An example of a commercial vinyl-acrylic latex spiked with 2% Texanol, 0.05% toluene, and 0.05% odorless mineral spirits is given in *Figure* 3. It should be noted that the low level of hydrocarbons gives an approximately equivalent GC response to that of the much higher level of the ester-alcohol Texanol.

Solvents found in water-based systems which are not detected by SPME include diethylene glycol and dibutyl phthalate. Solvents which give a weak, but a detectable SPME response, include ethylene glycol (EG), propylene glycol (PG), dipropylene glycol (DPnG) and diethylene glycol monomethyl ether (DM). All other alcohols, ketones, glycol ethers, and Texanol give a moderate strong SPME response and are therefore easily identified. In general, as the molecular weight and hydrophilicity of a solvent increases, its SPME response decreases.

A few of the solvents in water-based coatings have similar retention times (nearly identical retention indexes). Examples include ethylene glycol monobutyl ether (EB) and hexylene glycol (HG) with retention indexes of 661 and 662, respectively, and ethylene glycol mono-2-ethylhexyl ether (EEH) and propylene glycol monophenyl ether (PPh) with identical retention indexes of 903. In these cases, definite identification may be made by SPME/mass spectrometry or by carrying out the analysis using a chromatography column with a different stationary phase. Chromatographic peak shapes also help to identify specific solvents. Hexylene glycol, for example, tends to give a slightly broad, tailing peak while EB tends to give a very narrow, non-tailing peak. Some solvents are easily identified by GC peak multiplicity. Texanol, PnP, PnB, DPnP and DPnB give characteristic double GC peaks while DPM gives a characteristic triple GC peak.

If the GC method is used for carrying out the total VOC content of coatings, the mis-identification of a solvent may have only a minor effect on the total VOC content of coatings, especially those containing two or more solvents. If the FID response factor of a mis-identified solvent is nearly the same as the actual solvent, there is no effect on the total calculated VOC content.

The SPME procedure was used primarily for qualitative identification of volatile paint components. We have used the procedure for the quantitative determination of selected solvents. Acetone, which has recently become an exempt solvent, for example, may be determined by mixing a known quantity of hexadeuteroacetone (acetone-d6) with a known quantity of an acetone-containing coating sample. The headspace of the acetone-d6 spiked coating is sampled by SPME and desorbed onto a 60 m × 0.25 mm DB-Wax capillary column. Acetone-d6 and acetone d0 give GC peaks with baseline separation on this column and the amount of acetone in the coating may be calculated from peak areas. We tested the procedure by spiking a non-acetone containing water-based varnish with 9.14% acetone. A one-gram sample of this spiked coating was injected into a 40 ml septum cap vial containing 4 mL of water, 86.6 mg of acetone-d6 was added, and the sample was mixed by hand and let stand for 15 min. The headspace was then sampled four times by SPME and analyzed by GC to give values of 8.98, 9.07, 9.14, and 9.21%, respectively, for the acetone content in this coating. The area response factor for acetone-d0 is 1.145 times that of an equal mass of acetone-d6. Other analytes which may be analyzed quantitatively in this manner include methanol, ethanol, isopropyl alcohol, benzene, toluene, and methylene chloride. Separation of dichloromethane-d0 from dichloromethane-d2 requires the use of a 100 m × 0.25 mm Petrocol[7] capillary column.

Direct Analysis of Coatings Samples

After identification of the solvents in a specific coating by SPME, a solution of that coating was prepared in either methanol or dimethylformamide. For coatings containing analyte solvents which elute near both the MeOH and DMF peaks, it was necessary to prepare two separate solutions. For solutions prepared in methanol, the internal standard 2-ethylhexanol (2-EH) was employed for calculating analyte concentrations. In this method, a 10.0 mL aliquot of methanol containing 0.1058 mg/mL of 2-EH was pipetted into a 20 ml screw-cap test tube with a Teflon-lined screw cap. Approximately 30 to 50 mg of the well-mixed coating was weighed to the nearest 0.1 mg, by difference, directly into the methanol

solution with a disposable polypropylene syringe. The screw cap was attached to the tube and shaken by hand for about one minute. The tube was then placed in a sonicator for 15 min and then centrifuged. This procedure gave an almost clear supernatant liquid for most coating samples, with the majority of the pigment (when present) at the bottom of the test tube.

For the analyses, a 30m × 0.32 mm SPB-1 capillary column was used. The GC was used in the non-split mode, with an injection port temperature of 240°C. The flame ionization detector (FID) was maintained at 260°C. The oven was programmed from an initial temperature of 50°C for two minutes, to 240°C at 20°C per minute. The final temperature was held for two minutes. The column head pressure was adjusted such that ethylene glycol had a retention time of approximately 2.5 min. For the analyses, splitless injections of 0.5 to 1.5 microliters of extract were used. In general, when analyte concentrations were below 0.5 mg/mL, good chromatographic peak shapes were obtained and the detector response was linear. When analyte concentrations were greater than 0.5 mg/mL, an aliquot of the extract was quantitatively diluted with methanol/2-EH and rechromatographed. The chromatogram for a water-based clear wood finish, formulated with an acrylic-polyurethane resin, and the corresponding SPME screening chromatogram are presented in *Figure* 4. The SPME screening run for this coating shows the presence of six solvents while the methanol solution run exhibits a peak for triethylamine in addition to the six solvents found by SPME. The triethylamine in this case was formed by resin decomposition in the GC injection port and was therefore not counted in performing the total VOC calculation.

The FID response factor relative to the internal standard was determined for all solvents found by chromatographing known mixtures of the internal standard and known solvents. The calculation method for direct GC runs may be expressed as:

$$\text{Analyte\%} = \left[\frac{(AA \times RF \times VS \times DF)}{(AIS \times WS)}\right] \times 100$$

where:
- AA = area response of analyte
- RF = response factor for analyte in mg analyte per area unit relative to the unit area of the internal standard in mg per mL
- VS = volume of MeOH/IS
- DF = dilution factor of MeOH/IS
- AIS = area response for internal standard
- WS = weight of sample in mg

For coatings containing the solvents methanol, ethanol, isopropyl alcohol, the isomeric butanols, and propylene glycol monomethyl ether, solutions were prepared in DMF containing propyl alcohol as an internal standard. This method was also used for water-based coatings that might contain acetone or methyl ethyl ketone. Propyl alcohol was used as internal standard because it was not found in the coatings we examined and because it gave a GC peak which is well separated from the other low boiling components. For this application DMF was selected as the solvent, based on its good solvency for polymeric and monomeric coating materials, and its boiling point of 153°C, which resulted in its elution from the GC column after the low boiling solvents. DMF is also the solvent used for determination of water in coatings by ASTM Method D 3792,[9] a GC method which detects water by thermal conductivity with isopropyl alcohol as internal standard. A recent EPA method for the determination of hazardous air pollutants (HAPs) also suggests DMF as a solvent for the GC determination of these substrates.[10]

The method used for sample preparation in DMF and gas chromatography was identical to that described earlier for methanol solutions with the following exceptions: the sample size and internal standard concentrations were increased by a factor of 10, the GC injection mode was changed from splitless to split, and the injection volume was increased to approximately three microliters.

Certain solvents are not detected, or are detected with difficulty, by SPME and are, therefore, identified and determined in the direct GC portion of the analysis scheme. These solvents include ethylene glycol, diethylene glycol, dipropylene glycol, and the phthalate esters.

Validation

In 1994 we reported a study on the VOC determination using EPA Method 24, modified by a distillation method for removing water from coatings, followed by

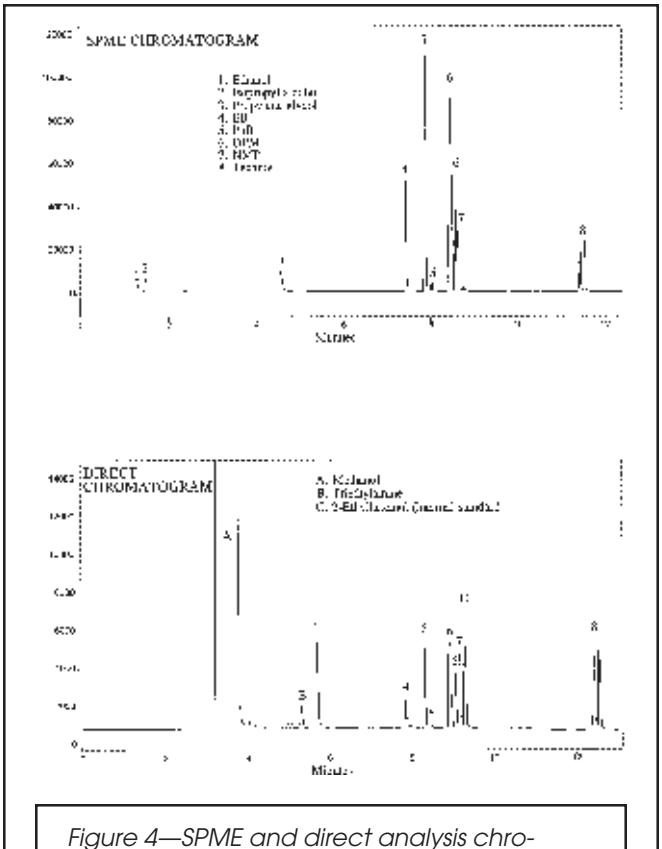

Figure 4—SPME and direct analysis chromatograms of a water-based clear wood finish.

Table 3—Direct GC Analysis of Known Paints and Comparison with Results Obtained in a Mini-Round Robin Using a Modified EPA Method 24

Sample	RS-052	RS-053	RS-054	RS-055	TP-06-02
% EG, GC					
Run #1	0.89	0.23	0.40	0.32	
Run #2	0.91	0.25	0.46	0.33	
Actual	*1.06*	*0.33*	*0.59*	*0.43*	
% TX, GC					
Run #1	1.22	0.32	0.60	0.45	1.79
Run #2	1.17	0.35	0.53	0.47	1.78
Actual	*1.06*	*0.33*	*0.59*	*0.43*	*1.63*
% MeOH, GC					
Run #1					1.98
Run #2					2.13
Actual					*2.13*
% DB, GC					
Run #1		6.81	11.62	0.06	
Run #2		7.01	11.60	0.07	
Actual		*6.92*	*11.08*	*0*	
% Total VOC, GC					
Run #1	2.11	7.36	12.62	0.83	3.77
Run #2	2.08	7.62	12.58	0.87	3.91
Actual	*2.12*	*7.58*	*12.26*	*0.86*	*3.76*
% Total VOC, found by	1.31	6.98	12.77	3.29	
EPA 24	2.35	6.41	11.60	0.93	
	1.57	6.55	12.58	1.57	
Water content, %	31.57	71.38	50.40	71.62	18.59
Coating VOC[a], *theory*	*59*	*383*	*375*	*55*	*92*
Coating VOC, GC	57	376	382	53	93
	56	384	381	55	96
Coating VOC, EPA 24[b]	37	379	393	182	
	66	403	368	59	
	44	350	368	90	

(a) Expressed as g/Liter minus water.
(b) Results obtained by three different laboratories.

Karl Fischer titration of the distillate.[11] In that study, we conducted a mini round-robin on four water-based latex paints which were prepared by Cardinal Industrial Finishes, South El Monte, CA. These paints were prepared in a manner that gave emphasis to the levels of water and co-solvent content such that either the water level was high, the VOC content was low or, as in one case, such that a single coating was both high in water content and low in VOC content. These same paints were analyzed in the present study using the direct GC procedure (*Table* 3). A traffic paint, TP-06-02 (obtained from the Rohm and Haas Company), containing known amounts of methanol and Texanol, was analyzed to validate the DMF extraction/direct GC method. In addition, one of the paints (RS-053) was spiked with additional ethylene glycol and with Texanol and a recovery study was performed (*Table* 4).

Table 4—Recovery Study of Ethylene Glycol and Texanol from RS 053 Spiked with 1% Each Componet

GC Run	% EG	% TX	% DB	% Total VOC Found
1	1.28	1.32	6.08	8.68
2	1.23	1.21	5.99	8.43
3	1.31	1.37	6.65	9.33
4	1.23	1.28	6.35	8.86
5	1.18	1.19	5.96	8.33
Average	1.25	1.27	6.21	8.73
Standard deviation	0.05	0.08	0.29	0.40
% Recovery	96	95	—	—
Actual	1.29	1.32	6.15	8.76

As the data of *Table* 3 show, the coating VOCs determined by gas chromatography are in excellent agreement with the theoretical VOC values and appear to be more reproducible than those obtained by EPA Method 24. The recovery studies of *Table* 4 show that the analysis by GC is not influenced in any significant way by a matrix effect and further show that the analysis is highly reproducible.

Paint Film Analysis

Parallel to our studies on the direct GC analysis of solvents in coatings, we evaluated a chamber method for determining solvent content. In this method the coating sample was placed into a modified one-quart paint can in which the can top was equipped with stainless steel fittings which allowed the released VOCs to be swept from the chamber by

Table 5—Analysis of Dried Paint Film from Chamber Run of RS-054

Component	Found in Sorbent, %	Found in Film, %	Total Found, %	Actual, %
EG	0.49	0	0.49	0.59
DB	10.33	0.36	10.69	11.08
TX	0.38	0.12	0.50	0.59
Total	11.20	0.48	11.68	12.26

a stream of ultra-high purity nitrogen to a manifold leading to multiple sorbent tubes containing a multisorbent. Glass beads (10 mm diameter) were placed into the can for the purpose of spreading a small quantity of coating over the bottom of the can. The chamber (paint can) was placed into a forced draft oven maintained at 110°C and purged for one hour, consistent with ASTM Method D 2369 for determination of nonvolatile content. The sorbed VOCs were then solvent extracted, followed by GC analysis of the resulting solutions. We found that coatings containing butyl carbitol (DB) and Texanol generally gave lower values of solvent concentrations by this chamber method than did the direct GC method (*Table* 5).

To explore the possibility that some high boiling solvents might remain associated with the film phase under certain conditions, we examined the dried paint film remaining in the sampling can after a chamber run of coating RS-054. The bottom of the can containing the paint film was removed, and a portion of the dried paint film was analyzed for residual solvent. The weighed film (about 200 mg) was sonicated for 30 min in 5 mL of acetone followed by the addition of 5.0 mL of methanol/2-EH and an additional 30 min of sonication. The sample was centrifuged, and the centrifugate was analyzed by GC, using our direct method. Analysis revealed that the dried paint film contained measurable amounts of butyl carbitol and Texanol, but no ethylene glycol. Using the known solids content of this sample (37.5%), the total amount of solvent trapped in the dried paint film could be calculated. Results are shown in *Table* 5. It is evident that these solvents remained in the paint film, even after the aggressive drying conditions (1 hr at 100°C) used in our chamber studies. It should be noted that a relatively large sample size (ca. 3.0 g), corresponding to a wet film thickness of about 8 mils, was used in this test. Normally, the chamber runs were conducted using coatings in the 0.50 g range. Clearly, the thicker the paint film, the more probable it is that higher boiling solvents will become associated with the film phase.

To test this phenomenon further, a commercial water-based semi-gloss coating known to have a fairly high Texanol content (TX, 2.9%) and a commercial water-based lacquer containing dibutyl phthalate (DBP, 0.99%) were tested for solids content by ASTM Method D 2369. The resulting dried films were recovered at various drying times then tested for residual solvent content as described previously. In addition, a sample of dioctyl phthalate (di-2-ethylhexyl phthalate, DOP, 100%) was tested as a neat liquid thin film. The results of this study are presented in *Table* 6. The amounts of Texanol and dibutyl phthalate remaining in the paint films were 24.1 and 84.5%, respectively, at the 60-min mark, which is the specified drying time of ASTM Method D 2369. If Texanol is counted as a VOC for the semi-gloss coating, the remaining 0.7% in the coating would contribute approximately 15 to 20 g to the coating VOC and give a smaller than actual VOC value if calculated by EPA Method 24 (ASTM Practice D 3960).

Gas Chromatographic Analysis of Commercial Water-Based Coatings

The water-based coatings analyzed by direct gas chromatography included 11 flat paints, nine low-gloss paints, 11 semi-gloss paints, four gloss paints, five wood stains, six traffic paints, four clear varnishes, one sanding sealer, and one water-reducible lacquer.[12] Twenty-three different solvents were found in these 52 coatings in amounts greater than 0.1% each by direct gas chromatography. Smaller amounts of a variety of different volatile substances, usually less than 0.1% total, could be identified by SPME in almost all of the coatings. These SPME identified minor components were not observed as measurable amounts of volatile substances by the direct GC method.

In order to assess the quality of information provided by existing literature sources, a number of comparisons were made between analytical results obtained in our laboratory, and information available on the Material Safety Data Sheets and Product Data Sheets for a number of coatings samples. During the analysis of these coatings samples, we generated quantitative composition information, which could be converted into VOC content, in grams per liter minus water. A comparison of manufacturer-provided VOC content with those calculated from our results is shown in *Table* 7. In general, the agreement between calculated and reported was good, with an average variation of five percent. In addition to the VOC content, we compared the actual species reported on MSDSs with those found by our analysis. There were cases in which components found by direct analysis were not reported on the MSDS and cases where a component reported on the MSDS was not found by direct analysis. We recognize that comparisons with

Table 6—Solvent Drying Study Using ASTM Method D 2369 of a Semi-Gloss Latex Paint, a Water-Based Lacquer, and Neat Dicotyl Phthalate

Time, min	% TX in Film, Semi Gloss	% DBP in Film, Lacquer	% DOP in Film, Neat DOP
0	2.90	0.99	100
30			99.4
40	0.90	0.87	
60	0.70	0.85	98.3
80	0.46	0.72	
90			97.7
100	0.24	0.65	

Table 7—VOC Comparison for Water-Based Coatings

Sample	Coating Type	VOC, Found	VOC, MSDS	Difference, %
WD-03	Gloss	241	215	12
WD-09	Flat	60	60	0
WD-10	Lo gloss	190	178	7
WD-11	Lo gloss	245	240	2
WD-12	Semi gloss	259	240	8
WD-13	Gloss	302	310	–3
WD-14	Stain	206	181	14
WD-15	Semi gloss	170	135	26
WD-16	Flat	168	200	–16
WD-17	Varnish	349	372	–6
WD-19	Clear gloss	290	227	28
WD-20	Stain	369	329	12
WD-21	Flat	199	160	24
WD-22	Lo gloss	170	165	3
WD-23	Semi gloss	258	244	6
WD-24	Semi gloss	218	209	4
WD-25	Flat	134	127	6
WD-26	Lo gloss	106	105	1
WD-27	Gloss	179	185	–3
WD-28	Flat	124	104	19
WD-29	Flat	153	141	9
WD-30	Semi gloss	124	116	7
WD-31	Flat	84	89	–6
WD-32	Lo gloss	122	121	1
WD-33	Semi gloss	249	241	3
WD-34	Semi gloss	223	219	2
WD-38	Traffic	59	55	7
WD-39	Lacquer	241	231	4
WD-40	Sanding sealer	234	231	1
WD-41	Traffic	141	139	1
WD-42	Traffic	69	70	–1
WD-43	Traffic	119	110	8
WD-44	Traffic	156	184	–15
WD-46	Gloss	238	250	–5
Average				5

MSDS data have limited value since MSDS data usually contain only enough information to satisfy regulatory requirements.

A detailed direct GC analysis result of one of the 52 coatings is presented in *Table* 8. This coating is a water-based clear wood finish based on an acrylic-polyurethane resin and contains six different solvents. Both the SPME and direct GC chromatogram of the solvents in this coating are presented in *Figure* 4. A GC peak for triethylamine (TEA) was observed for this coating in both the sorbent tube sampling of the VOCs and the direct injection of the coating in methanol. The sorbent tube sampling subjected the coating to a temperature of 110°C for one hour and showed the presence of 0.25% TEA. The direct injection of the coating solution in methanol subjected the soluble portion of the coating to a temperature of 240°C and showed the presence of 0.66% TEA. Since TEA was not observed by SPME sampling of the head space of this coating at room temperature, and is normally observed by SPME when present as the free amine, it was concluded that the TEA peak resulted from decomposition of the TEA-neutralized resin at elevated temperatures. TEA was, therefore, not included in the total VOC calculation for this coating, which resulted in an average VOC value of 302 g/L-water. Inclusion of TEA in the VOC calculation gave a coating VOC value of 306 g/L-water at the 0.25%. TEA level and a value of 313 g/L-water at the 0.66% TEA level.

Table 8—Results of the Direct GC Analysis of a Water-Based Clear Wood Finish Based on Five Separate GC Runs

	Average	Standard Deviation	Coefficient of Variation[a]
% PG	2.38	0.07	3.02
% EB	0.48	0.01	1.87
% PnB	1.27	0.04	3.50
% DPM	4.36	0.05	1.13
% NMP	1.67	0.06	3.44
% TX	2.86	0.11	4.03
% Total VOC	13.01	0.19	1.50
% Solids	30.06		
% Water	56.93	0.19	0.34
Density	1000		
VOC[b], found	302	3	1.04
VOC[b], theory	310		

(a) The coefficient of variation in the standard deviation divided by the average and expressed as a percent.
(b) Expressed in grams per liter minus water.

The results of *Table* 8 show that the repeatability of direct GC runs can be very good. Statistically, the results show that the precision for the method is as good or better than the published precision values for ASTM Practice D 3960.[3,4] More important, the precision values are not dependent on other variables as they are in ASTM Practice D 3960, where the ability to obtain meaningful VOC values tends to be unreliable at high water levels and low VOC content. Since the direct GC determination is independent of the water and

nonvolatile content of a coating, the precision will remain constant even at high water levels and low VOC levels. In fact, the determination of low VOC content is expected to be even more precise than a high VOC content, no matter what the water or nonvolatile content of a coating might be.

SUMMARY

Almost all of the solvents which evaporate during cure of a coating may be identified by solid phase micro extraction. This technique is simple, in that minimal equipment and time are required to carry out the procedure, and elegant, in that all of the volatile solvents, including minor components, may be easily identified. The technique may be especially useful for identifying some hazardous air pollutants and for identifying exempt solvents. After identifying the solvents present in a specific coating by SPME, a methodology for direct determination of these solvents by direct gas chromatography is put in place. We have found that the direct GC determination of the major solvents in water-based coatings may be used for determining the total VOC content of coatings and that the precision for the analysis is as good or better than the current EPA Method 24 (ASTM Practice D 3960). This direct method may prove to be advantageous for low VOC coatings which may be difficult to analyze accurately by the existing EPA Method 24.

The SPME method may be used for the quantitative determination of acetone, methanol, ethanol, isopropyl alcohol, benzene, toluene, and methylene chloride by adding a known quantity of the same, but deuterated, solvent to a coating containing the solvent of interest. Since the vapor pressures of the deuterated and undeuterated solvents are nearly the same, and since the deuterated and undeutered solvents are separated with an appropriate capillary column, the head space of the coating may be sampled by SPME and the relative amounts of deuterated and undeuterted solvents in a know quantity of coating may be determined. This approach gives a clean chromatographic procedure and appears to give good accuracy.

Some solvents, including Texanol, diethylene glycol monobutyl ether (DB), and dibutyl phthalate are not completely lost when ASTM Method D 2369 is used to determine the volatile content of some coatings. The extent to which solvent evaporation occurs under the test conditions may be determined by GC analysis of the dried paint film. We suspect that other high boiling solvents in coatings may also exhibit this characteristic and are continuing to investigate this phenomenon. Coatings neutralized with triethylamine lose triethylamine when the coatings are subjected to the test conditions of ASTM D 2369 but do not appear to lose triethylamine when cured at ambient conditions. We believe that the triethylamine-neutralized resins decompose at elevated temperatures, which results in an increase of the measured VOC content of these coatings. Resins in coatings which are neutralized with other amines may exhibit this same behavior. Since it is possible to determine which solvents evaporate from a coating at ambient temperature by SPME and since some of these solvents may be determined quantitatively by SPME, and it is also possible to analyze cured films for residual solvent content, these methods represent new approaches to the analysis of VOC content of coatings.

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